Charge Ordering in Manganite and Ferrite Systems

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Charge orderings exist ubiquitously in strongly correlated materials and can be widely used in energy related applications, such as supercapacitors, multiferroic materials, etc. As a typical charge ordering system, LuFe₂O₄ possesses periodically arranged Fe²⁺ and Fe³⁺ ions in the FeO double layers. The triangle-shaped sublattice of Fe ions leads to the frustrated states for both spin and charge. [1,2] Here, two different types of charge orderings, coexisting in a single crystalline LuFe₂O₄ sample, were directly observed (Fig. 1) by taking advantage of the in-situ cooling transmission electron microscopy (TEM). Specifically, vectors of q₁ = (1/3, 1/3, 1/2) and q₂ = (1/3, 1/3, 1) can be assigned to express these two charge ordering configurations, respectively (Fig. 1(a) and (b)). According to the real-space atomic models for q₁ and q₂ (Fig. 1(c) and (d)), q₁ charge ordering features an antiferroelectric configuration, while q₂ has a ferroelectric arrangement. Considering the space symmetry of LuFe₂O₄, there exist three equivalent q vectors for both q₁ (q₁, q₁’, q₁’’) and q₂ (q₂, q₂’, q₂’’) leading to a net q₁t vector and a q₂t vector along c direction as depicted in Fig. 1(e). By selecting q₁ and q₂ diffraction spots, charge ordering domains of q₁ and q₂ can be seen in the dark field TEM images in Fig. 1 (f) and (g) at 90 K, respectively, which present the spatial separation. Since the magnetic properties and charge orderings share the same origin (from Fe ions) in the LuFe₂O₄ system, the magnetic domains and charge ordering domains should be coupled, which has been manifested by our recent low temperature Lorentz TEM experiments.[3]

YMn₂O₄, which is another strongly correlated material with the isomorphic structure, is unstable in nature but can be synthesized by pulsed laser deposition (PLD) method. In the sample where the YMn₂O₄ thin film grown on α-Al₂O₃ substrate, MnO double layer was observed to self-assemble at the interface (Fig. 2(a) and (b)). Since YMn₂O₄ holds a similar crystal structure with LuFe₂O₄, the charge ordering within the MnO double layer can be expected. The charge ordering state in MnO double layers with the Type 3 (CO3) configuration can be detected by electron energy-loss spectroscopy (EELS), which manifests quite different characteristics from the one in LuFe₂O₄ (shown Fig. 2(g)). Further density functional theory (DFT) calculation results confirm the lowest energy state of CO3 configuration. [4]

In conclusion, different types of charge orderings have been identified in both manganite and ferrite systems by multiple TEM techniques. Due to the different orbital occupancies of Fe and Mn, LuFe₂O₄ and YMn₂O₄ present different intrinsic charge ordering configurations. The Lorentz TEM studied in ferrite system reveals the fact that the magnetic phase separation is caused by the spatial separation of the charge ordering domain. The charge-spin coupling has thus been established. The novel charge ordering found in manganite is expected to enhance the global ferroelectricity, since the charge ordering ferroelectric polarization and the geometric polarization are aligned. Our results show the rich physical phenomenon related with charge orderings, which provides a new playground for the emergent science [5].

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Figure 1. TEM results and atomic models for two different types of charge orderings in LuFe2O4 system. (a) (b) Selected area electron diffraction (SAED) patterns for q1 and q2 charge orderings, respectively, acquired at 90 K along [-110] direction. (c)(d) The conceived unit cells for the two types of charge orderings. Antiferroelectric configuration for q1, ferroelectric configuration for q2. (e) The resultant qt vector with the consideration of the symmetry of LuFe2O4 unit cell. (f) (g) Low magnification dark field TEM images of the distributions of two types of charge ordering domains of q1 and q2 accordingly.

Figure 2. TEM results and atomic models of the charge ordering in manganite systems. (a) HAADF-STEM image showing the interface between YMnO3 film and α-Al2O3 substrate along [210] direction. A reconstructed MnO double layer can be found at the interface, making a nominal YMn2O4 layer. The
atomic model of YMnO$_3$ is embedded. (b) HAADF image taken along [110] direction showing the interfacial reconstruction. (c)(d) Two different initial configurations ST1 and ST2 for DFT calculations. ST1 has longer Mn-Otp bonds in sublayer 2 than in sublayer 1, whereas ST2 has the reversed case. (e)-(h) Four different types of charge orderings in MnO double layers for DFT calculations. CO3 has the lowest energy among all these four configurations. The blue arrows indicate the geometric ferroelectricity, while the pink arrows indicate the ferroelectricity contributed from charge ordering.

References
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